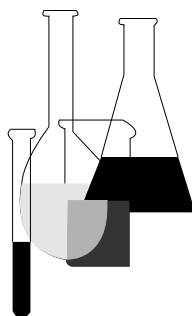




Fate, Transport and Transformation Test Guidelines

OPPTS 835.2210

Direct Photolysis Rate in Water By Sunlight



INTRODUCTION

This guideline is one of a series of test guidelines that have been developed by the Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency for use in the testing of pesticides and toxic substances, and the development of test data that must be submitted to the Agency for review under Federal regulations.

The Office of Prevention, Pesticides and Toxic Substances (OPPTS) has developed this guideline through a process of harmonization that blended the testing guidance and requirements that existed in the Office of Pollution Prevention and Toxics (OPPT) and appeared in Title 40, Chapter I, Subchapter R of the Code of Federal Regulations (CFR), the Office of Pesticide Programs (OPP) which appeared in publications of the National Technical Information Service (NTIS) and the guidelines published by the Organization for Economic Cooperation and Development (OECD).

The purpose of harmonizing these guidelines into a single set of OPPTS guidelines is to minimize variations among the testing procedures that must be performed to meet the data requirements of the U. S. Environmental Protection Agency under the Toxic Substances Control Act (15 U.S.C. 2601) and the Federal Insecticide, Fungicide and Rodenticide Act (7 U.S.C. 136, *et seq.*).

Final Guideline Release: This guideline is available from the U.S. Government Printing Office, Washington, DC 20402 on *The Federal Bulletin Board*. By modem dial 202-512-1387, telnet and ftp: fedbbs.access.gpo.gov (IP 162.140.64.19), or call 202-512-0132 for disks or paper copies. This guideline is also available electronically in ASCII and PDF (portable document format) from EPA's World Wide Web site (<http://www.epa.gov/epahome/research.htm>) under the heading "Researchers and Scientists/Test Methods and Guidelines/OPPTS Harmonized Test Guidelines."

OPPTS 835.2210 Direct photolysis rate in water by sunlight.

(a) **Scope**—(1) **Applicability.** This guideline is intended to meet testing requirements of both the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C. 136, *et seq.*) and the Toxic Substances Control Act (TSCA) (15 U.S.C. 2601).

(2) **Background.** The source material used in developing this harmonized OPPTS test guideline is 40 CFR 796.3700 Photolysis in Aqueous Solution in Sunlight.

(b) **Introduction**—(1) **Background and purpose.** Numerous chemicals enter natural aquatic systems from a variety of sources. For example, chemical wastes are discharged directly into natural water bodies, and chemicals leach into natural water bodies from landfills. Pesticides are applied directly into water bodies, and are applied to soils and vegetation, and subsequently leach into water bodies. Pollutants present in aqueous media can undergo photochemical transformation in the environment (i.e. in sunlight by direct photolysis or by sensitized photolysis). As a result, there is considerable interest in photolysis in solution, especially the photolysis of pesticides. However, most of these studies have been qualitative in nature and involved the identification of photolysis products. Quantitative data in the form of rate constants and half-lives are needed to determine the importance of photochemical transformation of pollutants in aqueous media. This test method describes a two-tiered screening level approach for determining direct photolysis rate constants and half-lives of chemicals in water in sunlight.

(2) **Definitions and units.** The definitions in section 3 of TSCA and in 40 CFR Part 792—Good Laboratory Practice Standards (GLP) apply to this test guideline. The following definitions also apply to this test guideline.

Absorbance (A_λ) is the logarithm of the ratio of the initial intensity (I_0) of a beam of radiant energy to the intensity (I) of the same beam after passage through a sample at a fixed wavelength λ . Thus, $A_\lambda = \log(I_0/I)$.

The *Beer-Lambert law* states that the absorbance of a solution of a given chemical species, at a fixed wavelength, is proportional to the thickness of the solution (l), or the light pathlength, and the concentration of the absorbing species (C).

Direct photolysis is the direct absorption of light by a chemical followed by a reaction which transforms the parent chemical into one or more products.

A *first-order reaction* is a reaction in which the rate of disappearance of a chemical is directly proportional to the concentration of the chemical

and is not a function of the concentration of any other chemical present in the reaction mixture.

The Grotthus-Draper law, the first law of photochemistry, states that only light which is absorbed can be effective in producing a chemical transformation.

The *half-life* ($t_{1/2}$) of a chemical is the time required for the concentration of the chemical being tested to be reduced to one-half its initial value.

Molar absorptivity (ϵ_λ) is the proportionality constant in the Beer-Lambert law when the concentration is given in terms of moles per liter (i.e. molar concentration). Thus, $A_\lambda = \epsilon_\lambda Cl$, where A_λ and ϵ_λ represent the absorbance and molar absorptivity at wavelength λ and l and C are defined in (3). The units of ϵ_λ are $\text{molar}^{-1} \text{ cm}^{-1}$. Numerical values of molar absorptivity depend upon the nature of the absorbing species.

Radiant energy, or radiation, is defined as the energy traveling as a wave unaccompanied by transfer of matter. Examples include X-rays, visible light, UV light, radio waves, etc.

The *reaction quantum yield* (ϕ_λ) for an excited-state process is defined as the fraction of absorbed light that results in photoreaction at a fixed wavelength λ . It is the ratio of the number of molecules that photoreact to the number of quanta of light absorbed or the ratio of the number of moles that photoreact to the number of einsteins of light absorbed at a fixed wavelength λ .

The *solar irradiance in water* (L_λ) is related to the sunlight intensity in water and is proportional to the average light flux (in the units of $10^{-3} \text{ einsteins cm}^{-2} \text{ day}^{-1}$) that is available to cause photoreaction in a wavelength interval centered at λ over a 24-hour day at a specific latitude and season date.

The *Stark-Einstein law*, the second law of photochemistry, states that only one molecule is activated to an excited state per photon or quantum of light absorbed.

The *sunlight direct aqueous photolysis rate constant* (k_{pE}) is the first-order rate constant in the units of day^{-1} and is a measure of the rate of disappearance of a chemical dissolved in a water body in sunlight.

A glossary of symbols can be found under paragraph (c)(5) of this guideline.

(3) Principle of the test method. (i) This test method is based on the principles developed by Zepp and Cline under paragraph (e)(8) of this guideline, Zepp under paragraph (e)(11) of this guideline, Mill et al. under paragraphs (e)(4), (e)(5), and (e)(6) of this guideline, and Dulin and Mill under paragraph (e)(2) of this guideline.

(ii) Zepp and Cline, under paragraph (e)(8) of this guideline published a paper on the rates of direct photolysis in aquatic environments. The rates of all photochemical processes in a water body are affected by solar spectral irradiance at the water surface, radiative transfer from air to water, and the transmission of sunlight in the water body. It has been shown that for photolysis of a chemical in an optically thin aqueous solution, the kinetics of direct photolysis can be described by the following equations:

Equation 1

$$\ln (C_0/C_t) = k_{pE}t$$

Equation 2

$$t_{1/2E} = 0.693/k_{pE}$$

Equation 3

$$k_{pE} = \phi_E k_a$$

where ϕ_E is the reaction quantum yield of the chemical in dilute solution and is independent of the wavelength, $k_a = \sum k_{a\lambda}$, the sum of $k_{a\lambda}$ values of all wavelengths of sunlight that are absorbed by the chemical (i.e. the light absorption rate constant), t is the time, C_0 and C_t are the concentrations of chemical at $t = 0$ and t , and $t_{1/2E}$ represents the half-life. The term k_{pE} represents the first-order photolysis rate constant for a water body in sunlight in the units of reciprocal time.

(iii) Furthermore, under the same conditions cited above, the first-order direct photolysis rate constant, k_{pE} , is given by the following equation:

Equation 4

$$k_{pE} = \phi_E \sum \epsilon_{\lambda} L_{\lambda}$$

where ϕ_E is the reaction quantum yield, ϵ_{λ} is the molar absorptivity in the units $\text{molar}^{-1} \text{ cm}^{-1}$, L_{λ} is the solar irradiance in water in the units of $10^{-3} \text{ einsteins cm}^{-2} \text{ day}^{-1}$ [Mill et al. under paragraph (e)(5) of this guideline], and the summation is taken over the range $\lambda = 290$ to 800 nm . L_{λ} is the solar irradiance at shallow depths for a water body under clear sky conditions and is a function of latitude and season of the year.

(iv) The method of Zepp and Cline under paragraph (e)(8) of this guideline and the method of Mill et al. under paragraph (e)(5) of this guideline are applicable to sunlight incident on a water surface such as natural water body. However, the method developed in this guideline measures rate constants in tubes (e.g. $13 \times 100 \text{ mm}$) and the rate is faster

in tubes. This is discussed in more detail in paragraph (c)(2)(i)(J) of this guideline. Thus, equations 1 and 2 have to be modified to take this into account. For simplicity, the following nomenclature is used. For water bodies, the rate constant is designated as k_{pE} with the subscript E designating rates in the environment in water bodies. For tubes, the rate constant is designated as k_p . The corresponding half-lives for water bodies and tubes are $t_{1/2E}$ and $t_{1/2}$, respectively. Thus, for tubes, equations 1 and 2 can be written as:

Equation 5

$$\ln(C_0/C_t) = k_p t$$

Equation 6

$$t_{1/2} = 0.693/k_p$$

(v) A simple first-tier screening test has been developed using Equation 4 under paragraph (b)(3)(iii) of this guideline. As an approximation, it is assumed that the reaction quantum yield ϕ_E is equal to one, the maximum value. As a result, the upper limit for the direct photolysis sunlight rate constant in aqueous solution is obtained and Equation 4 under paragraph (b)(3)(iii) of this guideline becomes

Equation 7

$$(k_{pE})_{\max} = \sum \epsilon_{\lambda} L_{\lambda}$$

Using equation 7 in equation 2 under paragraph (b)(3)(ii) of this guideline, the lower limit for the half-life is then given by

Equation 8

$$(t_{1/2E})_{\min} = 0.693/(k_{pE})_{\max}$$

The molar absorptivity can be determined experimentally by the method outlined in paragraph (c)(1) of this guideline and values of L_{λ} are given in Tables 3 to 6 as a function of latitude and season of the year under paragraph (c)(3) of this guideline. These data can then be used in equation 7 to calculate $(k_{pE})_{\max}$. Finally, $(k_{pE})_{\max}$ can then be substituted in Equation 8 to calculate $t_{1/2E})_{\min}$.

(vi) In a second-tier test method, an aqueous photolysis screening test has been developed to determine rate constants and half-lives in the presence of sunlight using Equations 1, 2, 4, 5, and 6 (Mill et al. under paragraphs (e)(4), (e)(5) and (e)(6) of this guideline, and Dulin and Mill under paragraph (e)(2) of this guideline). The second-tier test method is divided into two phases. In phase one, the test chemical is photolyzed in sunlight in order to obtain an approximate rate constant, k_{c_p} . This method only

gives an approximate rate constant since it fails to measure sunlight intensities incident on the sample during photolysis.

(vii) In phase two, a standard *p*-nitroacetophenone-pyridine actinometer (PNAP/PYR) is used to measure sunlight intensities incident on the sample during photolysis (Mill et al. under paragraph (e)(6) of this guideline and Dulin and Mill under paragraph (e)(2) of this guideline). The rate constant for this actinometer, k_p^a , can be adjusted to match the approximate rate constant of the test chemical by adjusting the concentration of pyridine. Since the rate constant is a function of the reaction quantum yield of the actinometer, the rate constant can be adjusted according to the equation

Equation 9

$$\phi_E^a = 0.0169[\text{PYR}]$$

where [PYR] is the molar concentration of pyridine for a *p*-nitroacetophenone (PNAP) concentration of 1.00×10^{-5} M. The reaction quantum yield for the test chemical, ϕ_E^c , is given by

Equation 10

$$\phi_E^c = \frac{k_p^c \sum \phi_\lambda^a L_\lambda}{k_p^a \sum \phi_\lambda^c L_\lambda} \phi_E^a$$

The reaction quantum yield of the test chemical, ϕ_E^c , can be determined in the following way. By measuring the concentration of test chemical and actinometer (PNAP) as a function of time *t* in sunlight, the ratio of rate constants, (k_p^c/k_p^a), can be determined using Equation 5 under paragraph (b)(2)(i)(H) of this guideline. The reaction quantum yield ϕ_E^a can be determined from Equation 9 at the molar concentration of pyridine used in the standard actinometer. The term $\sum \phi_\lambda^a L_\lambda$ for the actinometer has been tabulated as a function of latitude and season of the year in Table 2 under paragraph (c)(3) of this guideline. The term $\sum \phi_\lambda^c L_\lambda$ for the test chemical can be obtained from the experimentally measured molar absorptivities under paragraph (b)(1) of this guideline and the values of L_λ listed in Tables 3 to 6, as a function of latitude and season of the year under paragraph (c)(3) of this guideline.

(viii) With the values of ϕ_E^c , ϵ_λ^c , and the appropriate L_λ values, k_{pE} for the test chemical can be calculated as a function of latitude and season of the year in the United States using Equation 4 under paragraph (b)(3)(iii) of this guideline. The corresponding half-life can be calculated using k_{pE} in Equation 2 under paragraph (b)(3)(ii) of this guideline.

(4) **Applicability and specificity.** (i) This test method is applicable to all chemicals which have UV/visible absorption maxima in the range of 290 to 800 nm. Some chemicals have absorption maxima significantly below 290 nm and consequently cannot undergo direct photolysis in sunlight (e.g. chemicals such as alkanes, alkenes, alkynes, saturated alcohols, and saturated acids). This is a direct consequence of the Grotthus-Draper law. Some chemicals have absorption maxima significantly below 290 nm but have measurable absorption tails above the baseline in their absorption spectrum at wavelengths greater than 290 nm. Photolysis experiments should be carried out for these chemicals.

(ii) These test methods are only applicable to pure chemicals and not to the technical grade.

(iii) The first-tier screening test can be employed to estimate $(k_{pE})_{\max}$ and $(t_{1/2E})_{\min}$. If these data indicate that aqueous photolysis is an important process relative to other transformation processes (e.g. biodegradation, hydrolysis, oxidation, etc.), then it is recommended that the second-tier photolysis tests be carried out to determine environmentally relevant rate constants and half-lives in sunlight. The data obtained from this test can be used to determine k_{pE} for the test chemical as a function of latitude and season of the year anywhere in the United States. These rate constants are in a form suitable for preliminary mathematical modeling for environmental fate of a test chemical.

(iv) The second-tier screening test is applicable to the direct photolysis of chemicals in a homogeneous dilute solution with absorbance less than 0.05 in the reaction cell at all wavelengths greater than 290 nm and at shallow depths (less than 0.5 m). These results are applicable to direct sunlight photolysis for water bodies and clear sky conditions. In addition, these experiments are limited to the direct photolysis of chemicals in air-saturated pure water.

(v) This screening test has been designed to determine the molar absorptivity of a test chemical, ϵ_{λ}^c , and its reaction quantum yield, ϕ_{cE} . These parameters can be used to determine environmentally relevant rate constants at low absorbance and shallow depths in pure water as a function of latitude and season of the year. Tables of solar irradiance (Tables 3 to 6) under paragraph (c)(3) of this guideline have been included in this test method to carry out all the calculations. However, the method is really very general and can be extended to determine the rates of photolysis over a range of other environmental conditions using a computer program. Zepp and Cline under paragraph (e)(8) of this guideline have written a computer program to calculate the rates of photolysis as a function of depth in water, as a function of the attenuation coefficient of the water (α_{λ}) for natural water bodies, the average ozone layer thickness that pertains to the seasons and location of interest, and as a function of latitude and season of the year. This program has been recently updated with the best available solar

irradiance data and is called the GC SOLAR program. The GC SOLAR computer program is available on request as referenced under paragraph (e)(10) of this guideline.

(c) **Test procedures—(1) Tier 1 Test: UV/visible absorption spectra-estimation of aqueous photolysis maximum rate constant and minimum half-life in sunlight.** The UV/visible absorption spectra in aqueous solution can be determined by the methods described in OPPTS 830.7050. It is recommended that the following additional procedures be followed:

(i) For chemicals which ionize or protonate (e.g. carboxylic acids, phenols, amines), carry out UV/visible absorption studies at pHs at least two orders or magnitude above the pK_a and at least two orders of magnitude below the pK_a . Prepare buffer solutions at 25 °C using reagent grade chemicals and distilled water as follows: pHs in the range 3–6— NaH_2PO_4/HCl ; pHs in the range 6–8— $KH_2PO_4/NaOH$; pHs in the range >8—prepare buffers as described in the Handbook of Chemistry and Physics. In the case of pHs 3–6 and 6–8, use the minimum concentration of buffers to attain the desired pH. Check the pH of all the buffer solutions with a pH meter at 25 °C and adjust to the proper pH, if necessary. These buffer solutions can then be added to the test chemical solution until the desired pH is obtained. If these buffers are inadequate, then adjust the pH of the test chemical solution with 1 M HCl or NaOH at 25 °C.

(ii) (A) Measure the absorbance, A_λ , as a function of wavelength in the range of 290 to 800 nm in duplicate. If applicable, measure A_λ at each experimental pH. Record, in duplicate, the baseline when both the sample and reference cells are filled with blank solutions. These data will be used to calculate the molar absorptivities for the appropriate wavelength intervals and wavelength centers in Table 1 under paragraph (c)(3) of this guideline, where the test chemical absorbs light. The wavelength center is defined as the midpoint of the interval range.

(B) It must be emphasized that the molar absorptivities of the test chemical must be carefully determined, especially in the tails of the absorption bands at $\lambda \geq 290$ nm. Large errors will be encountered in calculating photolysis rate constants and half-lives if these measurements are not carefully carried out.

(2) **Tier 2 Test: Aqueous Photolysis in Sunlight—(i) Test conditions—(A) Special laboratory equipment.** It is recommended that quartz tubes be used for the photolysis of chemicals with appreciable absorption at wavelengths below 340 nm. Chemicals that absorb appreciably at wavelengths greater than 340 nm may be tested in borosilicate tubes. Thin-walled borosilicate or quartz tubes are recommended. Disposable culture tubes (13 × 100 mm) with Teflon-lined screw caps or quartz tubes with quartz or borosilicate stoppers, Teflon-lined, may be used as reaction ves-

sels. Tubes of 11 mm i.d. are recommended. For some chemicals, it may be difficult to determine the concentration of the test chemical in reaction tubes of small volume. For these chemicals, larger volume reaction vessels are recommended provided that the cell walls are thin and the pathlength of radiation through the vessel is less than 0.5 meter.

(B) **Purity of water.** Reagent grade water, e.g. water meeting ASTM Type II A standards, or an equivalent grade, is recommended to minimize biodegradation. ASTM Type II A water is described in ASTM D 1193–77—Standard Specification for Reagent Water. Air-saturated water can be easily prepared by allowing the water to equilibrate in a vessel plugged with sterile cotton. Copies may be obtained from the American Society for Testing and Materials (ASTM), 1916 Race Street, Philadelphia, PA 19103.

(C) **Sterilization.** It is extremely important to sterilize all glassware and to use aseptic conditions in the preparation of all solutions and in carrying out all photolysis experiments to eliminate or minimize biodegradation. Glassware can be sterilized in an autoclave or by any other suitable nonchemical method.

(D) **pH effects.** It is recommended that all photolysis experiments be carried out at pHs at least two orders of magnitude above the pK_a and at least two orders of magnitude below the pK_a for any chemical which ionizes or protonates (e.g. carboxylic acids, phenols, and amines). Buffers described in paragraph (b)(2)(ii)(B) of this guideline should be used.

(E) **Volatile chemical substances.** Special care should be taken when testing a volatile chemical so that the chemical substance is not lost due to volatilization during the course of the photolysis experiment. Thus, it is important to effectively seal the reaction vessels. Disposable culture tubes with Teflon-lined screw caps or quartz tubes with quartz or borosilicate stoppers, Teflon-lined, are recommended. Volatile compounds can be conveniently studied in culture tubes equipped with Mininert® valves. Samples can be introduced into or removed from the tubes through the septum in these valves with no loss of substrate. As an alternative, the tubes can be sealed with a torch. In addition, the reaction vessels should be as completely filled as is possible to prevent volatilization to any air space.

(F) **Control solution.** It is extremely important to take certain precautions to prevent loss of chemical from the reaction vessels by processes other than photolysis. For example, biodegradation and volatilization can be eliminated or minimized by use of sterile conditions and minimal air-space in sealed vessels. Hydrolysis is a process which cannot be minimized by such techniques. Thus, control vessels containing test substances which are not exposed to sunlight are required. In this way, the loss of test chemi-

cal for processes other than photolysis may be determined and eliminated. For simplicity, if the loss of chemical in the control is small (i.e. approximately 10 percent or less), one can calculate a first-order loss, k_{loss} , and subtract it from $(k_p)_{\text{obs}}$ to give the corrected direct photolysis rate constant k_p . If hydrolysis is found to be significant (i.e. greater than 10 percent), hydrolysis studies should be carried out first under OPPTS 835.2110.

(G) Absorption spectrum as a criterion for performing the aqueous photolysis test. This aqueous photolysis screening test is applicable to all chemicals which have UV/visible absorption maxima in the range of 290 to 800 nm. Some chemicals have absorption maxima significantly below 290 nm but have measurable absorption tails above the baseline in their absorption spectrum at wavelengths greater than 290 nm. Photolysis experiments should be carried out for these chemicals. The absorption spectrum of the chemical in aqueous solution can be measured by OPPTS 830.7050.

(H) Sunlight actinometer. (1) In order to quantify the rate of photolysis more precisely, it is necessary to measure the sunlight intensity incident on the sample during photolysis. A standard *p*-nitroacetophenone-pyridine actinometer (PNAP/PYR) has been developed (Mill et al. under paragraphs (e)(4) and (e)(6) of this guideline and Dulin and Mill under paragraph (e)(2) of this guideline) to measure the sunlight intensity incident on the sample during photolysis and this actinometer has been incorporated in this section. According to Equation 4 under paragraph (b)(3)(iii) of this guideline, the rate constant is a function of the reaction quantum yield. Furthermore, the reaction quantum yield can be adjusted by varying the molar concentration of the pyridine according to Equation 9 under paragraph (b)(3)(vii) of this guideline. Hence, by varying the pyridine concentration, the actinometer photolysis rate constant can be adjusted so that the half-life can range from several hours to several weeks. The initial concentration of PNAP is set at 1.00×10^{-5} M.

(2) Using the test chemical photolysis rate constant, k_p^c , determined in Tier 2, Phase 1, and the variable k_a^a ($= \sum \epsilon_{\lambda}^a L_{\lambda}$), listed in Table 2 under paragraph (c)(3) of this guideline the molar concentration needed to adjust the rate of disappearance of PNAP in PNAP/PYR to match the rate of disappearance of the test chemical is given by

Equation 11

$$[\text{PYR}] = 26.9 (k_p^c/k_a^a)$$

(3) Experiments are carried out by simultaneously photolyzing the test chemical and actinometer solutions. The concentrations of test chemical and actinometer are measured periodically as a function of time. These data are then used to determine the ratio of the rate constants, k_p^c/k_p^a , using linear regression analysis on the following equation:

Equation 12

$$\ln(C_o/C_t)^c = (k_p^c/k_p^a) \ln(C_o/C_t)^a$$

with $\ln(C_o/C_t)^a$ as the independent variable and $\ln(C_o/C_t)^c$ as the dependent variable. The slope of the best straight line is the ratio of the rate constants, k_p^c/k_p^a .

(I) Solar irradiance data. In order to calculate the reaction quantum yield of the test chemical, ϕ_E^c , and then calculate k_{pE}^c and $t_{1/2E}$, it is $t_{1/2E}$ necessary to use the solar irradiance parameter L_λ . L_λ values are proportional to the average light flux that is available to cause photolysis in a wavelength interval centered at λ over a 24-hour day at a specific latitude and season date. The L_λ values are defined by the angle of declination of the sun at -20° for winter, -10° for fall, $+10^\circ$ for spring, and $+20^\circ$ for summer. The actual dates for 1982 that correspond to these angles of declination are January 21, April 16, July 24, and October 20, for winter, spring, summer, and fall, respectively (AA (1982) under paragraph (e)(1) of this guideline). The L_λ values for these season dates are listed in Tables 3 to 6 under paragraph (c)(3) of this guideline as a function of latitude and are applicable to clear sky conditions, water bodies, shallow depths, and for chemicals whose absorbance is less than 0.05 in pure water (Mill et al. under paragraph (e)(7) of this guideline).

(J) Geometry of the reaction vessel. The method of Zepp and Cline under paragraph (e)(8) of this guideline and the method of Mill et al., under paragraph (e)(5) of this guideline are applicable to sunlight incident on a water surface such as a natural water body while the method developed in this test method measures rate constants (k_p) in tubes (e.g. 13×100 mm). However, rates in tubes are faster than in water bodies and it has been experimentally observed (Mill et al. under paragraph (e)(6) of this guideline) that

Equation 13

$$k_p = 2.2k_{pE}$$

Because tubes are the simplest and easiest reaction vessels to use, this test method recommends the use of tubes as reaction vessels and the method has been modified to take into account the increased rate in tubes (equation 13).

(K) Chemical analysis of solution. (I) In determining the concentration of the chemical in solution, an analytical method should be selected which is most applicable to the analysis of the specific chemical substance. Chromatographic methods are generally recommended because of their chemical specificity in analyzing the parent chemical substance without interference from impurities. Whenever practicable the chosen analytical method should have a precision of ± 5 percent or better.

(2) The *p*-nitroacetophenone in the chemical actinometer solution is conveniently analyzed by high-pressure liquid chromatography using a 30 cm C₁₈ reverse-phase column and a UV detector set at 280 nm. The mobile phase in volume percent is 2.5 percent acetic acid, 50 percent acetonitrile, and 47.5 percent water which is passed through the column at a flow rate of 2 mL/min.

(ii) **Preparations—(A) Preparation of test chemical solution.** Prepare homogeneous solutions with the chemical at less than one-half of its solubility in water and at a concentration such that the absorbance is less than 0.05 in the photolysis reaction vessel at wavelengths greater than 290 nm. For very hydrophobic chemicals, it is difficult and time consuming to prepare aqueous solutions. To facilitate the preparation of aqueous solutions containing very hydrophobic chemicals and to allow for easier analytical measurement procedures, the following procedure may be used to aid in the dissolution of the chemical. Dissolve the pure chemical in reagent grade acetonitrile. Add pure water as described under Test Conditions, in paragraph (b)(2)(i)(B) of this guideline, or buffer solution as described under Preparations, in paragraph (b)(2)(ii)(B) of this guideline, for chemical substances which ionize or protonate, to an aliquot of the acetonitrile solution. Do not exceed one volume-percent of acetonitrile in the final solution. Place the reaction solution in the appropriate photolysis reaction tubes as described in paragraph (b)(2)(i)(A) of this guideline.

(B) Preparation of buffer solutions. Prepare buffer solutions according to the procedures outlined in paragraph (b)(1)(i) of this guideline using reagent grade chemicals and pure water as described under Test Conditions, in paragraph (b)(2)(i)(B) of this guideline.

(C) Preparation of actinometer solution. (1) Using the test chemical photolysis rate constant, k_p^c , determined in Tier 2, Phase 1, and the variable k_a^a listed in Table 2 under paragraph (c)(3) of this guideline, the molar concentration of pyridine needed to adjust the rate of disappearance of *p*-nitroacetophenone (PNAP) to match the rate of disappearance of the test chemical can be obtained from equation 11 under paragraph (b)(2)(i)(H)(2) of this guideline. The variable k_a^a ($= \sum \epsilon_{\lambda}^a L_{\lambda}$) is equal to the day-average rate constant for sunlight absorption by PNAP which changes with season and latitude. The value of k_a^a is selected from Table 2 under paragraph (c)(3) of this guideline for the season nearest the mid-experiment date of the Tier 2, Phase 1, studies and the decadic latitude nearest the latitude of the experimental site.

(2) Once the molar concentration of pyridine [PYR] has been determined, an actinometer solution can be prepared as follows. Dissolve 0.165 gm. of PNAP in 100 mL of acetonitrile (0.01 M). Add 1 mL of this solution to a 1-L volumetric flask. Add to the volumetric flask the mass in grams, or the volume (V) of pyridine at 20° C, obtained from the equations

Equation 14

$$\text{mass(grams)} = 79.1 \text{ [PYR]}$$

$$V(\text{mL}) = 80.6 \text{ [PYR]}$$

Fill the volumetric flask with pure water as described in paragraph (b)(2)(i)(B) of this guideline to give 1 L of solution and shake vigorously to make sure that the solution is homogeneous. The PNAP/PYR solution should be wrapped with aluminum foil and kept from bright light.

(iii) **Performance of the tests—(A) Phase 1 experiments.** (1) For all experiments, prepare an aqueous solution of the chemical substance, as described in paragraph (b)(2)(i)(A) of this guideline, and a sufficient number of samples in quartz or borosilicate glass tubes to perform all the required tests. Fill the tubes as completely as possible and seal them. Prepare two control samples in the absence of UV light and totally exclude light by wrapping the tubes with aluminum foil or by other suitable methods. These samples are analyzed for the chemical substance immediately after completion of the experiment to measure the loss of chemical in the absence of light. Place the samples, including the controls, outdoors in an area free of shade and reflections of sunlight from windows and buildings. Place the samples on a black, nonreflective background and inclined at approximately 30° from the horizontal with upper end pointing due north (in the northern hemisphere). Conduct the photolysis experiments during a frost-free time of year (e.g. May, June, July, August, or September in the northern hemisphere—weather permitting) and start the experiments initially at noon (1200 hours). Record the date and time the experiment was begun, the date and time completed, the time of sunrise and sunset on all days when photolysis experiments were performed, the times exposure was stopped and restarted for intermittent exposure, the weather conditions during the period, and the latitude of the site. For chemical substances that ionize or protonate, carry out photolysis experiments at the required pHs as described under Test Conditions under paragraph (b)(2)(i)(D) of this guideline.

(2) If a significant loss of test chemical has occurred in the control samples, determine the cause and eliminate or minimize the loss. If hydrolysis is found to be significant, hydrolysis studies should be carried out first under paragraph (b)(2)(i)(F) of this guideline.

(3) Use one of the following procedures, depending on how fast the chemical substance photolyzes.

(i) **Procedure 1.** If the chemical substance transforms 50 to 80 percent within 28 days, measure the concentration of the chemical substance, in duplicate, at time $t = 0$ and periodically (at least four data points at approximately equal time intervals) at noon (1200 hours) until at least 50 percent of the substance has been consumed. As a simplification, the sam-

pling times can be estimated as the photolysis experiments progress. Determine the concentration of test chemical from two, freshly opened, reaction tubes for each time point. Determine the concentration in each of the two control solutions as soon as the photolysis experiments are completed.

(ii) **Procedure 2.** If the chemical substance transforms in the range of 20 to 50 percent in 28 days, determine the concentration of the chemical substance, in duplicate, at time $t = 0$. Determine the concentration of the chemical in the two separate reaction tubes and the two control tubes after 28 days of photolysis.

(iii) **Procedure 3.** For chemical substances that transform in sunlight 50 to 80 percent within one or two days, place the samples outside at noon (1200 hours) and analyze two samples for the concentration of the chemical substance at $t = 0$, and in two, freshly opened, reaction tubes at noon (1200 hours) the next day, and again, in two, freshly opened, reaction tubes at noon (1200 hours) the second day. Determine the concentration of the test chemical in each of the two control solutions after the first day of photolysis and as soon as the photolysis experiments have been completed on the second day.

(iv) **Analytical methodology.** Select an analytical method which is most applicable to the analysis of the specific chemical being tested under paragraph (b)(2)(i)(K) of this guideline.

(B) **Phase 2 experiments.** (1) Using the test chemical photolysis rate constant, k_c , determined in Tier 2, Phase 1, prepare an actinometer solution, as described in paragraph (b)(2)(ii)(C) of this guideline and a sufficient number of samples in quartz tubes to perform all the required tests. Fill all the tubes as completely as possible, seal them, and cover them with aluminum foil as soon as possible after preparation. Prepare an aqueous solution of test chemical, as described in paragraph (b)(2)(ii)(A) of this guideline, and a sufficient number of samples in quartz or borosilicate tubes to perform all the required tests. Fill these tubes as completely as possible, seal them, and cover them with aluminum foil as soon as possible after preparation. Place all the samples outdoors in an area free of shade and reflections of sunlight from windows and buildings. Place the samples on a black, nonreflective background and inclined at approximately 30° from the horizontal with the upper end pointing due north (in the northern hemisphere). Remove the foil from all samples except for the test chemical control solutions and the actinometer control solutions at noon (1200 hours). Based on the results of the Phase 1 experiments, determine the concentration of test chemical and actinometer (PNAP), in triplicate, at time $t = 0$ and periodically (at least five data points at approximately equal time intervals). Determine the concentration of PNAP in the three actinometer control solutions and the concentration of test chemical in the three control solutions for each time point.

(2) Select an analytical method which is most applicable to the analysis of the specific chemical tested, in paragraph (b)(2)(i)(K) of this guideline and follow the procedure given in paragraph (b)(2)(i)(K) of this guideline for the analysis of PNAP.

(d) Data and reporting—(1) Tier 1 Test: UV/visible Absorption Spectra—Estimation of Aqueous Photolysis Maximum Rate Constant and Minimum Half-Life in Sunlight—(i) Treatment of results. (A) The molar absorptivity can be determined from the absorption spectra using the expression.

Equation 15

$$\epsilon_{\lambda}^c = A_{\lambda}/Cl$$

where A_{λ} is the absorbance at wavelength λ , C is the molar concentration of test chemical, and l is the cell pathlength in centimeters. The molar absorptivity of the chemical should be determined for the wavelengths listed in Table 1 under paragraph (d)(3) of this guideline for a solution of concentration C and in a cell with pathlength, l . If the absorption curve is flat within the interval around the wavelength λ_{center} , ϵ_{λ} may be determined from the absorbance A_{λ} at λ_{center} using equation 15. If a large change in absorbance occurs within this interval, obtain an average absorbance A_{λ} at λ_{center} based on the absorbances at the two boundaries of the interval. Calculate an average ϵ_{λ} using the average value of A_{λ} in equation 15. Determine the molar absorptivity for each replicate and calculate a mean value.

(B) Using the molar absorptivities obtained from the spectra and the values of the L_{λ} from Tables 3 to 6 under paragraph (d)(3) of this guideline, the maximum rate constant $(k_{\text{pE}})_{\text{max}}$ can be calculated at a specific latitude and season of the year using equation 7 under paragraph (b)(3)(v) of this guideline. The minimum half-life, $(t_{1/2\text{E}})_{\text{min}}$ can then be calculated using this $(k_{\text{pE}})_{\text{max}}$ in equation 8 under paragraph (b)(3)(v) of this guideline.

(C) Two hypothetical examples are presented in paragraph (d)(4)(i) of this guideline to illustrate how the test data obtained in the first-tier screening test can be used.

(ii) Test data report. (A) Submit the original chart, or photocopy, containing a plot of absorbance of test chemical vs. wavelength plus the baseline. Spectra should include a readable wavelength scale, preferably marked at 10 nm intervals. Each spectrum should be clearly marked with the test conditions.

(B) Report the concentration of the test chemical solution, the type of absorption cell used (quartz or borosilicate glass) and the pathlength.

- (C) Report A_λ and ϵ_λ at λ_{center} for each replicate and the mean value.
- (D) Report $(k_{\text{pE}})_{\text{max}}$ and $(t_{1/2\text{E}})_{\text{min}}$ for the summer and winter solstices using the appropriate L_λ values from Tables 3–6 closest to the latitude of the chemical manufacturing site.
- (E) Report the identity and composition of the solvent used in the spectral absorption study.
- (F) For ionizable chemicals, report its pK_a . Report the type and concentration of the buffers employed for each pH. Report the pHs in which the photolysis experiments were carried out.
- (G) Describe the method used in determining the concentration of the test chemical.
- (H) Report the name, structure, and purity of the test chemical.
- (I) Submit a recent test spectrum on appropriate reference chemicals for photometric and wavelength accuracy.
- (J) Report the name and model of the spectrophotometer used.
- (K) Report the various control settings employed with the spectrophotometer. These might include scan speed, slit width, gain, etc.
- (2) Tier 2 Test: Aqueous photolysis in sunlight—(i) Phase 1 experiments—(A) Treatment of results.** (I) If a small loss of test substance in the control tubes has occurred, use this data to make corrections to the measured photolysis rate in paragraph (b)(2)(i)(F) of this guideline. Note the site of photolysis and its latitude and the weather conditions. For Procedures 1 and 2 note the dates and times of actual exposure including times of sunrise and sunset and, in case the cells are moved to prevent freezing or for other reasons, make sure that these times are recorded and that the cells are kept in a dark place when exposure is not in progress.
- (i) For chemical substances which transform 50 to 80 percent within 28 days, use a concentration C_t , which corresponds to less than 50 percent of the initial concentration of chemical substance remaining, and the corresponding time t , in days, along with the initial molar concentration C_0 , in Equation 5 to calculate k_p in days^{-1} . From the analysis of the two samples at time $t = 0$ and t , calculate a mean value of C_0 and C_t , respectively, and a value of k_p . If a slight loss of chemical has been detected in the controls, then calculate a rate constant as follows: Calculate an average concentration C_t , based on the duplicate measurements of concentration in the controls. Use this concentration along with the average initial concentration in Equation 5 and calculate a rate constant k_{loss} . Using this rate constant along with the observed rate constant, the corrected rate constant is then

Equation 16

$$k_p = (k_p)_{\text{obs}} - k_{\text{loss}}$$

Calculate the half-life, $t_{1/2}$ using the corrected k_p value in Equation 6 under paragraph (b)(3)(iv) of this guideline.

(ii) For chemical substances which transform 20 to 50 percent in 28 days, use the mean concentration C_t remaining at $t = 28$ days along with the mean value of C_0 to calculate k_p . Use the same procedure as described above to calculate the value of k_p and $t_{1/2}$. If less than 20 percent of the chemical substance degrades in 28 days, report the mean concentration of C_t and C_0 . In this case the apparent half-life is reported as greater than 3 months.

(iii) For chemical substances which transform 50 percent or more in the first day, as described in Procedure 3, calculate a full day k_p value using the mean concentration C_t of chemical substance remaining at noon (1200 hours) after the first day along with the mean value of C_0 using Equation 5 under paragraph (b)(3)(iv) of this guideline. For chemical substances which degrade less than 50 percent at noon (1200 hours) after the first day but 50 percent or more at noon (1200 hours) the second day, calculate k_p using the mean concentration of chemical substances remaining at noon (1200 hours) the second day. Calculate the half-life, $t_{1/2}$, using the mean value of k_p in Equation 6 under paragraph (b)(3)(iv) of this guideline. If a small loss of test substance in the control tubes has occurred, use this data to make corrections to the measured photolysis rate as described. Note the dates of photolysis, the latitude, and the site.

(2) A hypothetical example is presented in paragraph (d)(4)(ii) of this guideline, to illustrate how the test data obtained in the Tier 2, Phase 1, test method can be used.

(B) Specific analytical and recovery procedures. (1) Provide a detailed description or reference for the analytical procedures used, including the calibration data and precision.

(2) If extraction methods were used to separate the solute from the aqueous solution, provide a description of the extraction method as well as the recovery data.

(C) Other test conditions. (1) Report the size, approximate cell wall thickness, and type of glass used for the reaction tubes.

(2) Report the initial pH of all test solutions, if appropriate.

(3) For all procedures, report the dates of photolysis, the time of sunrise and sunset on each photolysis day, the site of photolysis and its latitude, and the weather conditions. For Procedures 1 and 2 submit the dates and times of actual exposure, and the duration of exposure, and, for inter-

mittent exposure, the fraction of each day during which photolysis occurred.

(4) If acetonitrile was used to solubilize the test substance, report the percent, by volume.

(5) If a significant loss of test chemical occurred in the control solution, indicate the causes and how they were eliminated or minimized.

(D) **Test data report.** (1) For each photolysis experiment, report:

(i) The initial molar concentration of test chemical (C_0) of each replicate and the mean value.

(ii) The molar concentration of test chemical for each replicate and the mean value for each time point t .

(iii) The molar concentration of each replicate control sample and the mean value after completion of the photolysis experiments.

(2) For Procedure 1, 2, or 3, report the value of k_p . If small losses of chemical are observed, report $(k_p)_{\text{obs}}$, k_{loss} and k_p . Report the half-life ($t_{1/2}$) calculated using the value of k_p .

(ii) **Phase 2 experiments—(A) Treatment of results.** (1) The objectives of this set of experiments is to determine the sunlight reaction quantum yield, $\phi^{\text{c}}_{\text{E}}$, for a specific test chemical. $\phi^{\text{c}}_{\text{E}}$ can be calculated using Equation 10 under paragraph (b)(3)(vii) of this guideline,

$$\phi^{\text{c}}_{\text{E}} = \frac{k^{\text{c}}_{\text{p}} \sum \phi^{\text{a}}_{\lambda} L_{\lambda}}{k^{\text{a}}_{\text{p}} \sum \phi^{\text{c}}_{\lambda} L_{\lambda}} \phi^{\text{a}}_{\text{E}}$$

by the following steps:

(i) Determine the ratio of the rate constants, $k^{\text{a}}_{\text{p}}/k^{\text{c}}_{\text{p}}$, as described in paragraph (b)(2)(i)(H) of this guideline using Equation 12. If a slight loss of test chemical or actinometer (PNAP) was detected in the controls at any time t , then employ the following procedure. Consider, as an example, the loss of test chemical in the control at time t . Using the average concentration of the test chemical in the controls from the replicates at time t and the average initial concentration, calculate $\ln(C_0/C_t)^{\text{c}}_{\text{loss}}$. Using the average concentration of test chemical from the replicates after photolysis time t , calculate $\ln(C_0/C_t)^{\text{c}}_{\text{obs}}$. The corrected term is then

Equation 17

$$\ln(C_0/C_t)^{\text{c}}_{\text{corr}} = \ln(C_0/C_t)^{\text{c}}_{\text{loss}}$$

The same procedure can be applied to obtain a corrected term from the actinometer (PNAP). Using the corrected terms for test chemical and/or actinometer in Equation 12 under paragraph (b)(2)(i)(H)(3) of this guideline, determine the ratio of the rate constants (k_p^a/k_p^c) as described in paragraph (b)(2)(i)(H) of this guideline.

(ii) Determine the quantum yield of the actinometer, ϕ_E^a , using Equation 9 and the molar concentration of pyridine [PYR] present in the actinometer.

(iii) Determine the value of $\sum \epsilon_\lambda^c L_\lambda$ for the test chemical as follows: the molar absorptivities, ϵ_λ , have been determined by the procedure given in paragraph (b)(1) of this guideline and the results have been tabulated according to paragraph (d)(1)(ii) of this guideline. Choose the appropriate L_λ values (Tables 3 to 6 under paragraph (d)(3) of this guideline) that correspond to the season closest to the season in which the Phase 2 experiments were performed and to the latitude nearest the latitude of the experimental site. Calculate the product of ϵ_λ and L_λ for each wavelength interval where ϵ_λ has a nonzero value. Sum the products of $\epsilon_\lambda L_\lambda$ over all wavelength intervals.

(iv) Determine the value of $\sum \epsilon_\lambda^a L_\lambda$ for the actinometer, as follows: These values have been calculated and are given in Table 2 under paragraph (d)(3) of this guideline. Choose the appropriate value that corresponds to the season closest to the season in which the Phase 2 experiments were performed and to the latitude nearest the latitude of the experimental site.

(v) Substitute the values of k_p^a/k_p^c , ϕ_E^a , $\sum \epsilon_\lambda^a L_\lambda$, and $\sum \epsilon_\lambda^c L_\lambda$ in Equation 10 under paragraph (b)(3)(iii) of this guideline and calculate ϕ_E^c , the quantum yield of the test chemical in the environment (i.e. in sunlight).

(2) Once ϕ_E^c has been determined, equation 4 under paragraph (b)(3)(iii) of this guideline can be used to calculate k_{pE} at any season of the year and latitude using the measured values of the molar absorptivities, ϵ_λ , and the appropriate L_λ values (Tables 3 to 6 under paragraph (d)(3) of this guideline). The half-life can then be calculated using k_{pE} in Equation 2 under paragraph (b)(3)(ii) of this guideline.

(3) A hypothetical example is presented in paragraph (d)(4)(iii) of this guideline, to illustrate how the test data obtained in the Tier 2, Phase 1, test method can be used.

(B) Other test conditions. (1) Report the size, approximate cell wall thickness, and type of glass used for tubes to hold the test chemical and actinometer solutions.

(2) Report the initial pH of all test chemical solutions, if appropriate, and the type and concentration of the buffers employed for each pH.

(3) If acetonitrile was used to solubilize the test chemical, report the percent, by volume, of the acetonitrile, which was used.

(4) If significant loss of test chemical occurred in the control solution, indicate the causes and how they were eliminated or minimized.

(C) **Test data report.** (1) Report the initial molar concentration of chemical (C_0) of each replicate and the mean value.

(2) Report the initial molar concentration of PNAP and the molar concentration of pyridine used in the actinometer.

(3) Report the time and date the sunlight photolysis experiments were started, the time and date the experiments were completed, and the elapsed photolysis time in days.

(4) For each time point, report the three separate values for the molar concentration of test chemical and PNAP and the mean values.

(5) For each time point, report the three separate values of the molar concentration of test chemical and PNAP for the controls and the mean values.

(6) Tabulate and report the following data: t , $\ln(C_0/C_t)^c$, and $\ln(C_0/C_t)^a$. From the linear regression analysis, report the ratio of the rate constants, k_p^c/k_p^a , and the correlation coefficient.

(7) If loss of test chemical and/or actinometer was observed during photolysis, then report the data $\ln(C_0/C_t)_{\text{corr}}$, $\ln(C_0/C_t)_{\text{obs}}$, $\ln(C_0/C_t)_{\text{loss}}$ for the test chemical and/or actinometer at each time t . From the linear regression analysis of $\ln(C_0/C_t)^c_{\text{corr}}$ and $\ln(C_0/C_t)^a_{\text{corr}}$, report the ratio of the rate constants, k_p^c/k_p^a and the correlation coefficient.

(8) Report the reaction quantum yield of the actinometer (ϕ^a_E).

(9) Report the value of k_a^a for the actinometer corresponding to the season closest to the season in which the photolysis experiments were carried out and to the latitude nearest the latitude of the experimental site.

(10) Tabulate the values of λ_{center} , ϵ_{λ}^c , L_{λ} , and $\epsilon_{\lambda}^c L_{\lambda}$ for the test chemical corresponding to the season closest to the season in which the photolysis experiments were carried out and to the latitude nearest the latitude of the experimental site.

(11) Report the value $\Sigma \epsilon_{\lambda}^c L_{\lambda}$ for the test chemical from step 10.

(12) Report the reaction quantum yield of the test chemical.

(13) Report k_{pE} and $t_{1/2E}$ for the summer and winter seasons using the appropriate L_{λ} values from Tables 3–6 under paragraph (d)(3) of this guideline closest to the latitude of the chemical manufacturing site.

(14) For chemicals that ionize, report the data for steps 1–13 for the experiments at the required pHs.

(3) *Tables of solar irradiance and related tables.*

Table 1.—Wavelength Center and Intervals for L_λ

λ center (nm)	Interval from (nm)	Range to (nm)	$>\lambda$ (nm)
297.5	296.2	298.7	2.5
300.0	298.7	301.2	2.5
302.5	301.2	303.7	2.5
305.0	303.7	306.2	2.5
307.5	306.2	308.7	2.5
310.0	308.7	311.2	2.5
312.5	311.2	313.7	2.5
315.0	313.7	316.2	2.5
317.5	316.2	318.7	2.5
320.0	318.7	321.2	2.5
323.1	321.2	325.0	3.8
330.0	325.0	335.0	10.0
340.0	335.0	345.0	10.0
350	345.0	355.0	10.0
360	355.0	365.0	10.0
370	365.0	375.0	10.0
380	375.0	385.0	10.0
390	385.0	395.0	10.0
400	395.0	405.0	10.0
410	405.0	415.0	10.0
420	415.0	425.0	10.0
430	425.0	435.0	10.0
440	435.0	445.0	10.0
450	445.0	455.0	10.0
460	455.0	465.0	10.0
470	465.0	475.0	10.0
480	475.0	485.0	10.0
490	485.0	495.0	10.0
500	495.0	505.0	10.0
525	512.5	537.5	25
550	537.5	562.5	25
575	562.5	587.5	25
600	587.5	612.5	25
625	612.5	637.5	25
650	637.5	662.5	25
675	662.5	687.5	25
700	687.5	712.5	25
750	725.0	775.0	50
800	775.0	825.0	50

Table 2—Day Averaged Rate Constant (k_a^a)¹ for Sunlight Absorption by PNAP as a Function of Season and Decadic Latitude

Latitude (degrees north)	Season			
	Spring	Summer	Fall	Winter
20	515	551	409	327
30	483	551	333	233
40	431	532	245	139
50	362	496	154	64

$$^1k_a^a = \sum \epsilon_{\lambda}^a L_{\lambda} \text{ in day}^{-1}.$$

Table 3— L_{λ} Values for Latitude 20° N.^{1 2 3}

λ center (nm)	Spring	Summer	Fall	Winter
297.5	1.10(−4)	1.52(−4)	7.77(−5)	3.71(−5)
300.0	4.06(−4)	5.26(−4)	2.96(−4)	1.62(−4)
302.5	1.10(−3)	1.35(−3)	8.21(−4)	4.99(−4)
305.0	2.37(−3)	2.79(−3)	1.79(−3)	1.17(−3)
307.5	4.24(−3)	4.86(−3)	3.24(−3)	2.25(−3)
310.0	6.65(−3)	7.45(−3)	5.13(−3)	3.72(−3)
312.5	9.42(−3)	1.04(−2)	7.33(−3)	5.47(−3)
315.0	1.24(−2)	1.35(−2)	9.68(−3)	7.40(−3)
317.5	1.54(−2)	1.66(−2)	1.21(−2)	9.38(−3)
320.0	1.82(−2)	1.96(−2)	1.44(−2)	1.13(−2)
323.1	3.23(−2)	3.45(−2)	2.55(−2)	2.04(−2)
330.0	1.10(−1)	1.17(−1)	8.75(−2)	7.08(−2)
340.0	1.37(−1)	1.45(−1)	1.10(−1)	9.02(−2)
350.0	1.52(−1)	1.60(−1)	1.22(−1)	1.01(−1)
360.0	1.67(−1)	1.76(−1)	1.35(−1)	1.12(−1)
370.0	1.78(−1)	1.88(−1)	1.45(−1)	1.21(−1)
380.0	1.89(−1)	2.00(−1)	1.55(−1)	1.30(−1)
390.0	1.79(−1)	1.89(−1)	1.46(−1)	1.22(−1)
400.0	2.57(−1)	2.71(−1)	2.09(−1)	1.75(−1)
410.0	3.38(−1)	3.57(−1)	2.76(−1)	2.31(−1)
420.0	3.47(−1)	3.67(−1)	2.84(−1)	2.38(−1)
430.0	3.35(−1)	3.54(−1)	2.74(−1)	2.30(−1)
440.0	3.95(−1)	4.18(−1)	3.25(−1)	2.72(−1)
450.0	4.45(−1)	4.70(−1)	3.65(−1)	3.07(−1)
460.0	4.50(−1)	4.75(−1)	3.70(−1)	3.11(−1)
470.0	4.65(−1)	4.91(−1)	3.83(−1)	3.22(−1)
480.0	4.76(−1)	5.03(−1)	3.92(−1)	3.31(−1)
490.0	4.50(−1)	4.76(−1)	3.72(−1)	3.13(−1)
500.0	4.59(−1)	4.85(−1)	3.80(−1)	3.20(−1)
525.0	1.21	1.28	1.00	8.48(−1)
550.0	1.26	1.33	1.05	8.83(−1)
575.0	1.27	1.35	1.06	8.92(−1)
600.0	1.29	1.36	1.07	9.05(−1)
625.0	1.29	1.37	1.08	9.15(−1)
650.0	1.30	1.38	1.09	9.24(−1)

Table 3— L_{λ} Values for Latitude 20° N.^{1 2 3}—Continued

λ_{center} (nm)	Spring	Summer	Fall	Winter
675.0	1.30	1.38	1.09	9.27(−1)
700.0	1.29	1.36	1.08	9.21(−1)
750.0	2.48	2.62	2.08	1.78
800.0	2.38	2.51	2.00	1.71

¹ Units of L_{λ} are 10^{-3} einsteins cm^{-2} day^{-1} . Multiplication of L_{λ} by ϵ_{λ} in units of $\text{molar}^{-1} \text{cm}^{-1}$ gives rate constants in units of day^{-1}

² The second number in the columns in parenthesis is the power of ten by which the first number is multiplied.

³ Based on the GC SOLAR program.

Table 4— L_{λ} Values for Latitude 30° N.^{1 2 3}

λ_{center} (nm)	Spring	Summer	Fall	Winter
297.5	5.73(−5)	1.09(−4)	3.18(−5)	6.78(−6)
300.0	2.50(−4)	4.11(−4)	1.46(−4)	4.23(−5)
302.5	7.65(−4)	1.14(−3)	4.64(−4)	1.71(−4)
305.0	1.79(−3)	2.46(−3)	1.12(−3)	4.95(−4)
307.5	3.43(−3)	4.45(−3)	2.19(−3)	1.11(−3)
310.0	5.64(−3)	7.02(−3)	3.67(−3)	2.04(−3)
312.5	8.27(−3)	1.00(−2)	5.46(−3)	3.26(−3)
315.0	1.12(−2)	1.32(−2)	7.43(−3)	4.69(−3)
317.5	1.41(−2)	1.64(−2)	9.48(−3)	6.21(−3)
320.0	1.70(−2)	1.95(−2)	1.15(−2)	7.76(−3)
323.1	3.04(−2)	3.46(−2)	2.07(−2)	1.43(−2)
330.0	1.05(−1)	1.18(−1)	7.23(−2)	5.17(−2)
340.0	1.33(−1)	1.48(−1)	9.23(−2)	6.75(−2)
350.0	1.47(−1)	1.63(−1)	1.03(−1)	7.65(−2)
360.0	1.62(−1)	1.80(−1)	1.15(−1)	8.60(−2)
370.0	1.73(−1)	1.91(−1)	1.24(−1)	9.31(−2)
380.0	1.84(−1)	2.04(−1)	1.33(−1)	1.01(−1)
390.0	1.74(−1)	1.93(−1)	1.25(−1)	9.39(−2)
400.0	2.50(−1)	2.77(−1)	1.79(−1)	1.35(−1)
410.0	3.29(−1)	3.64(−1)	2.36(−1)	1.79(−1)
420.0	3.38(−1)	3.74(−1)	2.43(−1)	1.84(−1)
430.0	3.26(−1)	3.61(−1)	2.35(−1)	1.78(−1)
440.0	3.86(−1)	4.26(−1)	2.79(−1)	2.12(−1)
450.0	4.34(−1)	4.79(−1)	3.14(−1)	2.39(−1)
460.0	4.39(−1)	4.85(−1)	3.19(−1)	2.42(−1)
470.0	4.54(−1)	5.01(−1)	3.30(−1)	2.51(−1)
480.0	4.65(−1)	5.13(−1)	3.38(−1)	2.58(−1)
490.0	4.40(−1)	4.85(−1)	3.20(−1)	2.44(−1)
500.0	4.49(−1)	4.95(−1)	3.27(−1)	2.50(−1)
525.0	1.18	1.31	8.67(−1)	6.61(−1)
550.0	1.23	1.36	9.03(−1)	6.87(−1)
575.0	1.24	1.37	9.11(−1)	6.93(−1)
600.0	1.25	1.38	9.24(−1)	7.04(−1)

Table 4— L_{λ} Values for Latitude 30° N.^{1 2 3}—Continued

λ_{center} (nm)	Spring	Summer	Fall	Winter
625.0	1.26	1.39	9.34(−1)	7.15(−1)
650.0	1.27	1.40	9.45(−1)	7.27(−1)
675.0	1.28	1.40	9.48(−1)	7.32(−1)
700.0	1.27	1.39	9.42(−1)	7.31(−1)
750.0	2.44	2.67	1.82	1.41
800.0	2.34	2.57	1.75	1.37

¹ Units of L_{λ} are 10^{-3} einsteins $\text{cm}^{-2} \text{day}^{-1}$. Multiplication of L_{λ} by ϵ_{λ} in units of $\text{molar}^{-1} \text{cm}^{-1}$ gives rate constants in units of day^{-1} .

² The second number in the columns in parenthesis is the power of ten by which the first number is multiplied.

³ Based on the GC SOLAR program.

Table 5— L_{λ} Values for Latitude 40° N.^{1 2 3}

λ_{center} (nm)	Spring	Summer	Fall	Winter
297.5	1.85(−5)	6.17(−5)	7.83(−6)	5.49(−7)
300.0	1.06(−4)	2.70(−4)	4.76(−5)	5.13(−6)
302.5	3.99(−4)	8.30(−4)	1.89(−4)	3.02(−5)
305.0	1.09(−3)	1.95(−3)	5.40(−4)	1.19(−4)
307.5	2.34(−3)	3.74(−3)	1.19(−3)	3.38(−4)
310.0	4.17(−3)	6.17(−3)	2.19(−3)	7.53(−4)
312.5	6.51(−3)	9.07(−3)	3.47(−3)	1.39(−3)
315.0	9.18(−2)	1.22(−2)	4.97(−3)	2.22(−3)
317.5	1.20(−2)	1.55(−2)	6.57(−3)	3.19(−3)
320.0	1.48(−2)	1.87(−2)	8.18(−3)	4.23(−3)
323.1	2.71(−2)	3.35(−2)	1.51(−2)	8.25(−3)
330.0	9.59(−2)	1.16(−1)	5.44(−2)	3.16(−2)
340.0	1.23(−1)	1.46(−1)	7.09(−2)	4.31(−2)
350.0	1.37(−1)	1.62(−1)	8.04(−2)	4.98(−2)
360.0	1.52(−1)	1.79(−1)	9.02(−2)	5.68(−2)
370.0	1.63(−1)	1.91(−1)	9.77(−2)	6.22(−2)
380.0	1.74(−1)	2.04(−1)	1.05(−1)	6.78(−2)
390.0	1.64(−1)	1.93(−1)	9.86(−2)	6.33(−2)
400.0	2.36(−1)	2.76(−1)	1.42(−1)	9.11(−2)
410.0	3.10(−1)	3.64(−1)	1.87(−1)	1.20(−1)
420.0	3.19(−1)	3.74(−1)	1.93(−1)	1.24(−1)
430.0	3.08(−1)	3.61(−1)	1.87(−1)	1.20(−1)
440.0	3.65(−1)	4.26(−1)	2.22(−1)	1.43(−1)
450.0	4.11(−1)	4.80(−1)	2.51(−1)	1.61(−1)
460.0	4.16(−1)	4.85(−1)	2.54(−1)	1.64(−1)
470.0	4.30(−1)	5.02(−1)	2.63(−1)	1.69(−1)
480.0	4.40(−1)	5.14(−1)	2.70(−1)	1.74(−1)
490.0	4.16(−1)	4.86(−1)	2.56(−1)	1.65(−1)
500.0	4.25(−1)	4.96(−1)	2.62(−1)	1.68(−1)
525.0	1.12	1.31	6.93(−1)	4.45(−1)
550.0	1.16	1.36	7.21(−1)	4.61(−1)

Table 5— L_{λ} Values for Latitude 40° N.^{1 2 3}—Continued

λ_{center} (nm)	Spring	Summer	Fall	Winter
575.0	1.17	1.37	7.22(−1)	4.61(−1)
600.0	1.18	1.38	7.39(−1)	4.69(−1)
625.0	1.20	1.40	7.50(−1)	4.82(−1)
650.0	1.21	1.41	7.62(−1)	4.95(−1)
675.0	1.22	1.41	7.68(−1)	5.03(−1)
700.0	1.21	1.40	7.66(−1)	5.05(−1)
750.0	2.33	2.69	1.48	9.84(−1)
800.0	2.25	2.59	1.43	9.56(−1)

¹ Units of L_{λ} are 10^{-3} einsteins $\text{cm}^{-2} \text{ day}^{-1}$. Multiplication of $L_{\lambda} \epsilon_{\lambda}$ in the units of $\text{molar}^{-1} \text{ cm}^{-1}$ gives the rate constant in units of day^{-1} .

² The second number in the columns in parenthesis is the power of ten by which the first number is multiplied.

³ Based on the GC SOLAR program.

Table 6— L_{λ} Values for Latitude 50° N.^{1 2 3}

λ_{center} (nm)	Spring	Summer	Fall	Winter
297.5	3.61(−6)	2.86(−5)	9.58(−7)	5.47(−8)
300.0	3.05(−5)	1.50(−4)	8.27(−6)	4.17(−7)
302.5	1.54(−4)	5.33(−4)	4.47(−5)	2.62(−6)
305.0	5.24(−4)	1.39(−3)	1.63(−4)	1.34(−5)
307.0	1.32(−3)	2.89(−3)	4.39(−4)	5.14(−5)
310.0	2.66(−3)	5.05(−3)	9.32(−4)	1.49(−4)
312.5	4.53(−3)	7.75(−3)	1.66(−3)	3.43(−4)
315.0	6.82(−3)	1.08(−2)	2.58(−3)	6.52(−4)
317.5	9.34(−3)	1.40(−2)	3.64(−3)	1.07(−3)
320.0	1.19(−2)	1.71(−2)	4.76(−3)	1.57(−3)
323.1	2.25(−2)	3.12(−2)	9.19(−3)	3.39(−3)
330.0	8.26(−2)	1.10(−1)	3.48(−2)	1.45(−2)
340.0	1.09(−1)	1.40(−1)	4.71(−2)	2.12(−2)
350.0	1.22(−2)	1.57(−1)	5.43(−2)	2.53(−2)
360.0	1.36(−1)	1.74(−1)	6.18(−2)	2.96(−2)
370.0	1.47(−1)	1.86(−1)	6.76(−2)	3.30(−2)
380.0	1.57(−1)	1.99(−1)	7.37(−2)	3.65(−2)
390.0	1.48(−1)	1.87(−1)	6.89(−2)	3.49(−2)
400.0	2.12(−1)	2.69(−1)	9.90(−2)	4.98(−2)
410.0	2.80(−1)	3.55(−1)	1.31(−1)	6.54(−2)
420.0	2.89(−1)	3.65(−1)	1.35(−1)	6.71(−2)
430.0	2.79(−1)	3.52(−1)	1.31(−1)	6.47(−2)
440.0	3.31(−1)	4.17(−1)	1.55(−1)	7.66(−2)
450.0	3.73(−1)	4.69(−1)	1.75(−1)	8.62(−2)
460.0	3.78(−1)	4.75(−1)	1.78(−1)	8.74(−2)
470.0	3.90(−1)	4.91(−1)	1.84(−1)	8.95(−2)
480.0	4.00(−1)	5.03(−1)	1.89(−1)	9.15(−2)
490.0	3.78(−1)	4.76(−1)	1.79(−1)	8.62(−2)
500.0	3.86(−1)	4.85(−1)	1.83(−1)	8.77(−2)

Table 6— L_λ Values for Latitude 50° N.^{1 2 3}—Continued

λ_{center} (nm)	Spring	Summer	Fall	Winter
525.0	1.01	1.28	4.84(−1)	2.28(−1)
550.0	1.05	1.33	5.03(−1)	2.32(−1)
575.0	1.05	1.34	5.04(−1)	2.28(−1)
600.0	1.06	1.35	5.13(−1)	2.32(−1)
625.0	1.08	1.37	5.26(−1)	2.42(−1)
650.0	1.10	1.38	5.39(−1)	2.53(−1)
675.0	1.11	1.39	5.47(−1)	2.61(−1)
700.0	1.11	1.38	5.49(−1)	2.66(−1)
750.0	2.15	2.66	2.07	5.22(−1)
800.0	2.08	2.57	1.04	5.11(−1)

¹ Units of L_λ are 10^{-3} einsteins $\text{cm}^{-2} \text{ day}^{-1}$. Multiplication of L_λ by ϵ_λ in the units of $\text{molar}^{-1} \text{ cm}^{-1}$ gives the rate constant in units of day^{-1} .

² The second number in the columns in parenthesis is the power of ten by which the first number is multiplied.

³ Based on the GC SOLAR program.

(4) Examples of application of methodology—(i) Tier 1 Test: UV/visible absorption spectra—estimation of aqueous photolysis rate constant and minimum half-life in sunlight—(A) illustrative example 1.

A neutral organic chemical A was dissolved in water at a concentration of 1.00×10^{-3} M. UV/visible absorption spectra were obtained in a 10.0 cm quartz absorption cell and no absorbance was detected above the baseline in the region 290 nm and greater (i.e. $A_\lambda = 0$) for $\lambda \geq 290$ nm). Since $A_\lambda = 0$, then $\epsilon_\lambda^c = 0$ (Equation 15). Using this result in Equation 7, it is found that $(k_{pE})_{\text{max}} = 0$, indicating that no direct photolysis can take place in sunlight at any latitude or season of the year. This example illustrates the principle of the Grotthus-Draper law. That is, in order for direct photolysis to take place in sunlight, the chemical must absorb sunlight in the region $\lambda \geq 290$ nm.

(B) Illustrative example 2. (1) Consider a plant located in Columbus, Georgia on the Chattahoochee River which produces an organic chemical B which is not an acid or a base. The waste effluent passes through a primary and secondary treatment plant and is then discharged directly into the river. The plant produces chemical B continuously every day of the year. The plant is located at 32.5° north latitude. Estimate the maximum sunlight direct photolysis rate constant and the corresponding minimum half-life for this chemical in the river for the winter and summer seasons under clear skies.

(2) Laboratory experiments, data, and calculations: (i) The water solubility of chemical B is 1.00×10^{-3} M at 25 °C. Chemical B was dissolved directly in water and a 1.00×10^{-4} molar solution was prepared at 25 °C. The UV/visible absorption spectra were obtained according to the Tier 1 procedure in a 10.0 cm quartz absorption cell in duplicate. Using the

wavelength interval range (from Table 1 under paragraph (d)(3) of this guideline), the average absorbance of the duplicate runs at λ_{center} was obtained and the results are summarized in the following Table 7:

Table 7—Summary of Photolysis Data for Chemical B
Spectral Data

λ_{center} (nm)	A_{λ}	ϵ^c_{λ} (M ⁻¹ cm ⁻¹)
297.5	1.684	1684
300.0	1.434	1434
302.5	1.221	1221
305.0	0.919	919
307.5	0.742	742
310.0	0.208	208
312.5	0.138	138
315.0	0.094	94
317.5	0.057	57
320.0	0.009	9
323.1	0.002	2
330.0	0.000	0

Photolysis Data

λ_{center} (nm)	Summer		Winter	
	L_{λ}^1	$\epsilon_{\lambda}^c L_{\lambda}$ (day ⁻¹)	L_{λ}^1	$\epsilon_{\lambda}^c L_{\lambda}$ (day ⁻¹)
297.5	1.09(−4)	0.18	6.78(−6)	0.01
300.0	4.11(−4)	0.59	4.23(−5)	0.06
302.5	1.14(−3)	1.39	1.71(−4)	0.21
305.0	2.46(−3)	2.26	4.95(−4)	0.45
307.5	4.45(−3)	3.30	1.11(−3)	0.82
310.0	7.02(−3)	1.46	2.04(−3)	0.42
312.5	1.00(−2)	1.38	3.26(−3)	0.45
315.0	1.32(−2)	1.24	4.69(−3)	0.44
317.5	1.64(−2)	0.94	6.21(−3)	0.35
320.0	1.95(−2)	0.18	7.76(−3)	0.07
323.1	3.46(−2)	0.07	1.43(−2)	0.03
330.0	1.18(−1)	0.00	5.17(−2)	0.00
		$\epsilon_{\lambda}^c L_{\lambda} = 12.99$		$\epsilon_{\lambda}^c L_{\lambda} = 3.31$

¹ The units of L_{λ} are in 10⁻³ einsteins cm⁻² day⁻¹. The second number in the columns in parenthesis is the power of ten by which the first number is multiplied.

(ii) From the above data and Equation 15 under paragraph (d)(1)(i)(A) of this guideline, the average molar absorptivity is

Equation 18

$$\epsilon_{\lambda} = 1,000 A_{\lambda}$$

From the average A_λ value at λ center, the average molar absorptivity can be obtained from Equation 18 and the results are summarized in Table 7 under paragraph (d)(4)(i)(B)(2)(i) of this guideline. Since the plant is located at 32.5° north latitude, the closest L_λ values are at 30° north latitude. These values are obtained from Table 4 under paragraph (d)(3) of this guideline and are summarized in Table 8 under paragraph (d)(4)(i)(B)(2)(i) of this guideline for the summer and winter seasons. Using the data from Table 7 under paragraph (d)(4)(B)(2)(i) of this guideline and Equations 7 and 8 under paragraph (b)(3)(v) of this guideline, the following results are obtained.

Summer

$$(k_{pE})_{\max} = \sum \epsilon_\lambda C L_\lambda = 13.0 \text{ day}^{-1}$$

$$(t_{1/2E})_{\min} = 0.053 \text{ day}$$

Winter

$$(k_{pE})_{\max} = \sum \epsilon C L_\lambda = 3.31 \text{ day}^{-1}$$

$$(t_{1/2E})_{\min} = 0.21 \text{ day}$$

Since the chemical transforms rapidly for the summer and winter seasons, it is necessary to carry out Tier 2 experiments to more accurately define direct photolysis rates in aqueous media as a function of the season of the year.

(ii) **Tier 2 Phase 1: Aqueous photolysis in sunlight—illustrative example 3.** (A) Consider the same scenario as described in illustrative example 2, under paragraph (d)(4)(i)(B) of this guideline. Using the Tier 2, Phase 1 Procedure, carry out experiments to estimate the rate of direct photolysis and half-life in aqueous solution in the spring for water bodies.

(B) Photolysis experiments and calculations: Since chemical B absorbs appreciably below 340 nm, 11 mm i.d. quartz tubes were used (note: this tube has an approximate pathlength of 1 cm). Chemical B was dissolved directly in pure water and a 1.00×10^{-5} molar solution was prepared at 25°C . Since the water solubility is 1.00×10^{-3} M at 25°C , this sample solution was well below one-half its water solubility. The UV spectrum of this solution in a 1 cm absorption cell indicated that A_λ was less than 0.05 at 290 nm. Hence, under these conditions, first-order kinetics are applicable.

(C) A series of quartz tubes were filled with this aqueous solution, sealed, and photolysis experiments were carried out in sunlight according to the appropriate procedure described in paragraph (b)(2)(iii)(A) of this guideline. The experiments were started at noon (1200 hours) on May 8, 1982. The weather conditions are summarized for this period of time and

the concentration data given represent the mean of duplicate determinations.

(1) May 2, 1982: at $t = 0$ (noon—1200 hours) $C_0 = 1.00 \times 10^{-5}$ M.

(2) May 2, 1982: Noon to sunset—clear and sunny.

(3) May 3, 1982: Noon (1200 hours), $C_t = 0.840 \times 10^{-5}$ M.

(4) May 3, 1982: at 1400 hours the weather conditions were cloudy with rain. The rain and cloudy weather continued until 2200 hours.

(5) From sunrise, May 4, 1982 through 1200 hours May 8, 1982, the weather was clear and sunny. At 1200 hours, May 8, 1982, analysis of the samples gave an average concentration of $C_t = 0.400 \times 10^{-5}$ M. Since 60 percent of chemical B transformed, the photolysis experiments were terminated and the control samples were analyzed. The average concentration of the control samples was 0.997×10^{-5} M which was essentially the same as C_0 . Hence, no adventitious processes occurred and the loss of chemical was only due to sunlight photolysis.

(D) Listed in the following Table 8 are the times of sunrise and sunset for the dates sunlight photolysis experiments were carried out along with the total number of hours of sunlight.

Table 8—Summary of Times for Sunrise and Sunset for the Period May 2–8, 1982

Date (1982)	Sunrise (a.m.)	Sunset (p.m.)	Total sunlight hours
May 2	0600	2010	14.2
May 3	0559	2011	14.2
May 4	0558	2012	14.2
May 5	0557	2013	14.3
May 6	0556	2014	14.3
May 7	0555	2015	14.3
May 8	0554	2016	14.4

(E) The following data summarizes the dates photolyzed, the times exposed to sunlight, the total sunlight photolysis time for each date in days, the total number of days of sunlight photolysis, and the calculation of k^C_P and $t_{1/2}$.

Date	Times photolyzed	Sunlight photolysis time for each (days)
May 2	1200 to 2010 hours (8.2/14.2)	0.58
May 3	0559 to 1200 hours (6.0/14.2)	0.42
May 3	1200 to 1400 hours (2.0/14.2)	0.14
May 4	0558 to 2012 hours	1.00
May 5	0557 to 2013 hours	1.00
May 6	0556 to 2014 hours	1.00
May 7	0555 to 2015 hours	1.00
May 8	0554 to 1200 hours (6.1/14.4)	0.42

¹ Total hours.

$$t = 5.6 \text{ days}; C_0 = 1.00 \times 10^{-5}; C_t = 0.400 \times 10^{-5}$$

$$\ln(C_0/C_t) = k^C_P t$$

$$k^C_P = (1/t) \ln(C_0/C_t) = (1/5.6) \ln(1.00 \times 10^{-5}/0.400 \times 10^{-5})$$

$$k^C_P = 0.16 \text{ days}^{-1}$$

$$t_{1/2} = 0.693/0.16 \text{ days}^{-1} = 4.3 \text{ days}$$

Therefore, the rate constant for direct photolysis of chemical B in tubes in pure water is 0.16 days^{-1} and the corresponding half-life is 4.3 days for the period of photolysis May 2–8, 1982, at 32.5° north latitude. Using equation 13, under paragraph (b)(2)(i)(J) of this guideline, the direct photolysis rate constant (k_{PE}) for water bodies is 0.073 days^{-1} and the corresponding half-life ($t_{1/2E}$) is 9.5 days.

(iii) **Tier 2, Phase 2: Aqueous photolysis in sunlight—illustrative example 4.** (A) Consider the same scenario as described in illustrative examples 2 and 3. Using the Tier 2, Phase 2, procedure, carry out experiments to determine the sunlight reaction quantum yield and estimate the rate constant for direct photolysis in aqueous solution and the half-life for water bodies and clear sky conditions for the summer and winter seasons.

(B) Photolysis experiments and calculations: The sunlight photolysis experiments were carried out in the beginning of May 1982, at 32.5° north latitude.

(C) Preparation of the actinometer solution: (1) The results from the Tier 2, Phase 1, experiments indicated that K_c for the test chemical was 0.16 days⁻¹. Since the experiments were carried out in early May at 32.5° north latitude, the value of K_a was chosen from Table 2 which corresponds to the spring season and at 30° north latitude; and the value is 483 days⁻¹. Using Equation 11 under paragraph (b)(2)(i) (H) of this guideline, the molar concentration of pyridine required to adjust the actinometer rate to match the rate of disappearance of the test chemical is

$$[\text{PYR}] = 26.9 (0.16/483) = 8.91 \times 10^{-3} \text{ molar}$$

Using this concentration of pyridine, an actinometer solution was (ii)(C) prepared according to the procedure described in paragraph (b)(2) of this guideline. The quantum yield for this actinometer is calculated using equation 9 under paragraph (b)(3)(vii) of this guideline.

$$\phi^a_E = 0.0169[\text{PYR}] = 0.0169(8.91 \times 10^{-3}) = 1.51 \times 10^{-4}$$

(2) Procedures for Tier 2, Phase 2 experiments (under paragraph (b)(2)(iii) of this guideline) were followed and sunlight experiments were initiated at 1200 hours on May 9, 1982. The mean initial concentration of test chemical was 1.00×10^{-5} molar and the mean initial concentration of PNAP was 1.00×10^{-5} molar. Samples of the chemical and actinometer and the controls were analyzed in triplicate periodically at 1200 hours on May 10, 11, 13, 15, and 16. On May 16, the photolysis experiments were terminated. The mean concentrations of all samples are summarized as follows:

Date	Concentration of chemical (M)	Concentration of actinometer (M)	Concentration of chemical control (M)	Concentration of actinometer control (M)
May 9	1.00×10^{-5}	1.00×10^{-5}	1.00×10^{-5}	1.00×10^{-5}
May 10	0.820×10^{-5}	0.855×10^{-5}	0.997×10^{-5}	1.00×10^{-5}
May 11	0.654×10^{-5}	0.710×10^{-5}	1.00×10^{-5}	0.997×10^{-5}
May 13	0.440×10^{-5}	0.515×10^{-5}	0.996×10^{-5}	0.999×10^{-5}
May 15	0.299×10^{-5}	0.383×10^{-5}	0.999×10^{-5}	0.998×10^{-5}
May 16	0.233×10^{-5}	0.304×10^{-5}	0.997×10^{-5}	0.996×10^{-5}

Since no significant loss of PNAP or test chemical was observed in the control samples, no adventitious processes occurred and the loss of test chemical and PNAP was only due to sunlight photolysis.

(3) Using the above data, $\ln (C_o/C_t)$ for the test chemical and actinometer can be calculated and the results are summarized as follows:

t (days)	Chemical		Actinometer	
	$C_t \times 10^5$ (M)	$\ln (C_o/C_t)^c$	$C_t \times 10^5$ (M)	$\ln (C_o/C_t)^a$
0	1.00	0.000	1.00	0.000
1	0.820	0.199	0.855	0.157
2	0.654	0.425	0.710	0.343
4	0.440	0.821	0.515	0.664
6	0.299	1.21	0.383	0.960
7	0.233	1.46	0.304	1.19

(4) The ratio of the rate constants, k_p^c/k_p^a , is defined by equation 12 under paragraph (b)(2)(i)(H)(3) of this guideline.

Equation 12

$$\ln(C_o/C_t)^c = (k_p^c/k_p^a) \ln(C_o/C_t)^a$$

(5) Using all the data (including the time point $t = 0$) and linear regression analysis, the slope is found to be 1.237 with a correlation coefficient of 0.9998. Therefore,

$$(k_p^c/k_p^a) = 1.24$$

(6) Using the molar absorptivities obtained in example 2 under paragraph (d)(4)(i)(B) of this guideline and the L_λ values for spring at 30° north latitude in Table 4 under paragraph (d)(3) of this guideline, the value of $\sum \epsilon_\lambda L_\lambda$ can be calculated as follows:

λ center (nm)	$\epsilon_{\lambda}(\text{M}^{-1}\text{cm}^{-1})$	L_{λ}^{-1}	$\epsilon_{\lambda}L_{\lambda}$ (days ⁻¹)
297.5	1684	5.73 (-5)	0.10
300.0	1434	2.50 (-4)	0.36
302.5	1221	7.65 (-4)	0.93
305.0	919	1.79 (-3)	1.65
307.5	742	3.43 (-3)	2.55
310.0	208	5.64 (-3)	1.17
312.5	138	8.27 (-3)	1.14
315.0	94	1.12 (-2)	1.05
317.5	57	1.41 (-2)	0.80
320.0	9	1.70 (-2)	0.15
323.1	2	3.04 (-2)	0.06
330.0	0	1.05 (-1)	0.00

¹ The units of L_{λ} are 10^{-3} einsteins cm^{-2} day⁻¹.

$$\sum \epsilon_{\lambda} L_{\lambda} = 9.96 \text{ days}^{-1}.$$

For this experiment, $k_a(\sum \epsilon_{\lambda} L_{\lambda})$ is 483 days⁻¹ (Table 2 under paragraph (d)(3) of this guideline). All the pertinent data are summarized as follows:

$$k_p^c/k_p^a = 1.24$$

$$\sum \epsilon_{\lambda} L_{\lambda} = 9.96 \text{ days}^{-1}$$

$$\sum \epsilon_{\lambda}^a L_{\lambda} = 483 \text{ days}^{-1}$$

$$\phi_E^a = 1.51 \times 10^{-4}$$

Substituting these results into Equation 10 under paragraph (b)(3)(vii) of this guideline yields

$$\phi_E^c = (1.24)(483/9.96)(1.51 \times 10^{-4})$$

$$\phi_E^c = 9.08 \times 10^{-3}$$

(7) The rate constants for direct photolysis of test chemical in aqueous media and the half-life for water bodies and clear sky conditions for the winter and summer seasons can be calculated as follows: The values of $\sum \epsilon_{\lambda}^c L_{\lambda}$ have been calculated from example under paragraph (d)(3)(i)(A) of this guideline. For summer $\sum \epsilon_{\lambda}^c L_{\lambda} = 13.0 \text{ days}^{-1}$; for winter $\sum \epsilon_{\lambda}^c L_{\lambda} = 3.31 \text{ days}^{-1}$. The reaction quantum yield for the chemical is 9.08×10^{-3} . Using these data in equation 4 under paragraph (b)(3)(iii) of this guideline yields

Summer

$$k_{pE} = 9.08 \times 10^{-3} (13.0) = 0.118 \text{ days}^{-1}$$

Winter

$$k_{pE} = 9.08 \times 10^{-3} (3.31) = 0.0301 \text{ days}^{-1}$$

These values can be substituted into Equation 2 under paragraph (b)(3)(ii) of this guideline to obtain the half-lives for these two seasons.

Summer:

$$t_{1/2E} = (0.693/0.118) = 5.9 \text{ days}$$

Winter:

$$t_{1/2E} = (0.693/0.0301) = 23 \text{ days}$$

(5) Glossary of symbols

PYR = Pyridine.

PNAP = *p*-Nitroacetophenone.

λ = Wavelength λ .

A_λ = Absorbance at wavelength λ .

a = Actinometer (composed of PNAP/PYR).

ϵ^c_λ = Molar absorptivity of a chemical C .

ϵ^a_λ = Molar absorptivity of the actinometer.

l = light pathlength; the distance traveled by a beam of light passing through the system.

ϕ^c_E = Sunlight reaction quantum yield of chemical c in water.

ϕ^a_E = Sunlight reaction quantum yield of the actinometer in water. Since the reaction quantum yield is independent of λ , $\phi^a_E = \phi^a$ (i.e. the reaction quantum yield of the actinometer measured in the laboratory).

$[C]$ = Molar concentration of chemical c .

$[PYR]$ = Molar concentration of pyridine.

$-d[C]/dt$ = Direct photolysis rate of chemical c .

k_{pE} = Direct photolysis sunlight rate constant in water bodies in the environment.

$(k_{pE})_{\max}$ = Maximum direct photolysis sunlight rate constant in water bodies in the environment.

k^c_p = Direct photolysis sunlight rate constant of chemical c in water in tubes.

k_p^a = Direct photolysis sunlight rate constant of the actinometer in water in tubes.

$k_{a\lambda}$ = Specific light absorption of a photoreactive chemical at a low concentration and at wavelength λ .

k_a = Specific light absorption rate constant integrated over all wavelengths absorbed by the chemical.

k_a^a = Specific light absorption rate constant integrated over all wavelengths absorbed by the actinometer.

$t_{1/2}$ = Sunlight half-life of a chemical in water in tubes.

$(t_{1/2E})_{\min}$ = The minimum sunlight half-life of a chemical in water bodies in the environment.

I = The numbers of photons of light of wavelength λ in the system per cm^2 per second.

L_λ = Solar irradiance in water in the units 10^{-3} einsteins cm^{-2} day $^{-1}$.

γ = The geometry factor which represents the ratio of the rate constants in tubes (k_p) to the rate constant in water bodies in the environment (k_{pE}).

(e) **References.** For additional background information on this test guideline the following references should be consulted:

(1) *Astronomical Almanac* (1982).

(2) Dulin, D. and Mill, T. Development and application of solar actinometers. *Environmental Science and Technology* 16:815 (1982).

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(4) *Handbook of Chemistry and Physics*. (Chemical Rubber Company, Cleveland, OH)

(5) Mill, T. et al. *Evaluation and Optimization of Photolysis Screening Protocols*. EPA Report No. 560/5-81-003 (1981).

(6) Mill, T. et al. *Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water*. EPA Report No. 600/3-82-022 (1982).

(7) Mill, T. et al. *Design and Validation of Screening and Detailed Methods for Environmental Processes*.

(8) Zepp, R.G. and Cline, D.M. Rates of direct photolysis in aquatic environment. *Environmental Science and Technology* 11:359 (1977).

(9) Zepp, R.G. Quantum yields for reaction of pollutants in dilute aqueous solution. *Environmental Science and Technology*, 12:327 (1978).

(10) Zepp, R.G. Environmental Research Laboratory, U.S. Environmental Protection Agency, College Station Road, Athens, Georgia 30601.